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## Stability Study of some Fungicides and their Relevant Impurities in some Environmental Conditions

#### Seloma, A. S. O.\*



Pesticides Analysis Res. Dept., Central Agric. Pesticides Lab., Agric. Res. Center, Dokki, Giza, Egypt.

#### ABSTRACT



The effects of storage conditions on some fungicide pesticides, metalaxyl modified by mancozeb represented in acimaxyl 72% WP, and copper modified by mancozeb represented in triomax 66% WP were investigated. The results revealed that the degradation rates for acimaxyl 72% WP and triomax 66% WP differed during storage, with the calculated half-life values for acimaxyl being (149.48 days for mancozeb and 43.33 days for metalaxyl) and (113.64 days for mancozeb and 104.24 days for copper) in triomax. After 14 days at 54 °C, the effect of thermal storage on the synthesis of ethylene thiourea (ETU) in mancozeb was raised to 0.222% for acimaxyl and 0.160 % for triomax. Furthermore, the influence of oven temperature on storage 2,6 dimethyl aniline impurity in acimaxyl (mancozeb 64% and metalaxyl 8%) was 0.020% before storage and 0.040% at the end of the experiment storage time. Before and after storage at 54 °C, the levels of lead, cadmium, and arsenic (mg/kg) as well as metallic copper were measured in triomax 66% (mancozeb 12%, and copper 29%). The levels of cadmium and arsenic were fewer than FAO limits, whereas lead was more than FAO limits. The data showed that metallic copper in triomax formulation remained generally consistent over time.

Keywords: Fungicides, relevant Impurities, arsenic, cadmium, lead, copper.

#### INTRODUCTION

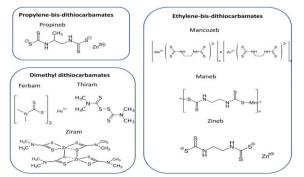
#### **Fungicides:**

The word fungicide is derived from two Latin words, fungus and caedo. The term caedo means to kill. Thus the fungicide is any agent or chemical capable of killing the fungus. According to this meaning, physical agents such as ultra violet light and heat should also be regarded fungicides in this sense. Ingeneral usage, however, only chemicals are included in the definition. As a result, fungicide is a chemical that can destroy fungi.

Fungicides are either synthetic or natural compounds that prevent parasites or infectious spores from growing. Fungicides do not kill parasites; instead, they halt their development for a few days or weeks. In agriculture, parasites can cause serious damage, resulting in production, quality, and profit losses. Fungicides are used in both horticulture and agriculture.Fungicides are used in horticulture as well as to combat infectious diseases in animals. Synthetics used to control oomycetes, which are not creatures, are also referred to as fungicides because oomycetes contaminate plants through parasitic systems similar to parasites (Latijnhouwers *et al.*, 2000).

#### Dithiocarbamate fungicides.

DTFs (dithiocarbamate fungicides) are nonsystemic pesticides that have been used to manage a variety of fungal infections in crops and ornamental plants since the 1940s. Some of the most well-known and widely used fungicides include propineb, zineb, maneb, thiram, and mancozeb, whose chemical structures are shown in Figure 1.



#### Figure 1. Classification of dithiocarbamate fungicides (DTF) and chemical structures of main representatives from each group.

Dithiocarbamate (DTC) fungicides are a class of organosulfur compounds with the general structure (R1R2) N-(C = S)-SX, where R can be an alkyl, alkylene, aryl, or similar other group, and X is usually a metal ion, that are widely used in agriculture and frequently detected as pesticide residues in plant products all over the world.

In natural science, a dithiocarbamate is a practical gathering. It's a carbamate in which both oxygen molecules are replaced by sulphur atoms (when just 1 oxygen is supplanted the outcome is thiocarbamate).

Since the 1940s, dithiocarbamates, specifically ethylene bisdithiocarbamates (EBDCs), have been commonly used as fungicides in farming as edifices with manganese (maneb), zinc (zineb), or a combination of manganese and zinc (mancozeb). A Short History of Fungicides" (2016). At the Joint FAO/WHO Meeting in 1967, the dithiocarbamate fungicides ferbam, mancozeb, maneb, nabam, thiram, zineb, and ziram were evaluated. Although biochemical data was limited, temporary adequate daily admissions (ADI's) were established for these mixes; however, it was noted that these ADI's must be suited to the parent intensities alone (FAO/WHO, 1968).

#### Mancozeb

Mancozeb is a non-fundamental dithiocarbamate agricultural fungicide with multi-site, contact-based defensive activity. Cornell University combines two other dithiocarbamates: maneb and zineb (1993) Cornell University(1993).

Mancozeb is a dithiocarbamate non-fundamental horticultural fungicide with multi-site, defensive activity on contact. It is a blend of two other dithiocarbamates: maneb and zineb. The combination protects a wide range of agricultural crops, organic products, nuts, vegetables, and ornamentals from a variety of infectious diseases. Penncozeb, Trimanoc, Vondozeb, Dithane, Manzeb, Nemispot, and Manzane are some of the names for it. As early as 2008, a combination of zoxamide and mancozeb was enrolled in Canada for the management of the mould Hammer. "Gowan purchases Dow's Hammer potato fungicide" (2008).

A minor amount of ethylene thiourea (ETU) is created during the production of mancozeb technical. In proper manufacturing practice, this should not exceed 0.5 % of the mancozeb at the time of manufacture. All mancozeb-containing goods should be stored in a cold, dry environment to avoid breakdown.

#### Copper fungicides.

Copper is a metal that has the potential to increase and decrease soil profitability, separation limit, and buffering limit (Andreu and Gimeno-Garcia, 1999). This could be even more of a concern in sensitive biological systems such as swamps or wetlands than in rice plantations. When metals, such as copper, are put to soil, they may: (a) remain in the soil arrangement and wash off in waste water, (b) be taken up by plants, or (c) be held in solvent or insoluble structures by the soil.Because of patterns of vigorous and anaerobic conditions impacting the soil redox potential, there is constant shift in the accessibility of metals in a framework that is occasionally moist and dry. This may render such soils impotent in the face of increased metal solvability and toxicity. (Andreu and Gimeno-Garcia, 1999). Copper is more portable (extractable) than cadmium, lead, zinc, nickel, or cobalt among the metals, although it is nevertheless kept in the ground for lengthy periods of time. In a study conducted over a five-year period in a rice-growing region of Spain, researchers showed that copper did, in any case, gradually drop over time, unlike cadmium, which has shown a proclivity to build up (Andreu and Gimeno-Garcia, 1999). Copper is found in the upper levels of the dirt profile, and its abundance decreases as depth increases.

Copper-based arrangements have been used to manage organisms and bacterial illnesses in developed plants for more than 200 years. Following the unintended publication of the Bordeaux combination in 1880, their use spread far and wide (Zwieten *et al.*, 2007). At that point, winegrowers in the Bordeaux wine locale were utilizing a combination of copper sulfate also, lime to hinder bystanders from eating the grapes, Millardet noticed that these grapes didn't give any indications of wool mold; and affirmed that this combination controlled this illness at moderately ease. Subsequently, Bordeaux blend turned into the first fungicide to be utilized for an enormous scope around the world (Schneiderhan, 1933).

A copper pesticide is a copper compound utilized as a pesticide or fungicide. In the UK the Dirt Affiliation (one of the natural certificate specialists) licenses ranchers to utilize some copper fungicides on natural land utilized for the creation of confirmed natural yields just if there is a significant danger to crops Soil Association Organic Standards for Producer (2010). The mixtures allowed are copper sulfate, copper hydroxide, cuprous oxide, copper oxychloride, copper ammonium carbonate (at a most extreme convergence of 25 g/l), and copper octanoate. As per the Dirt Affiliation the all-out copper that can be applied to natural land is 6kg/ha/year permitting application of copper fungicide of the Soil Association Archived (15 October 2009). This cutoff is planned so the measure of copper in the dirt doesn't surpass the cutoff points determined in the Dirt Affiliation norms for substantial metals.

The technical material and formulation of copper may contain cadmium, lead and arsenic which have to be regarded as relevant impurities FAO (1989 and 1998).

Cadmium, which enters the body through tainted food, is a toxin that affects the kidneys even at low levels of exposure. Industrial emissions and fertilizers are the main sources of cadmium in food. Because cadmium has a lengthy biological half-life, accumulation is ongoing. Chronic cadmium poisoning symptoms include emphysema of the lungs, minor liver damage, anemia proteinuria, renal tubular damage, and certain dental problems (UNEP/FAO/WHO 1986).

Lead is a cumulative poison which produces a series of effects on blood-forming tissues, the digestive and nervous systems, and the digestive and the kidneys. Lead exposures have developmental and neuro behavioral effects on fetuses, infants and children, and elevate blood pressure in adults. Also, people affected by lead poisoning become pallid, moody and irritable, their appetite fails and they may come anemic (UNEP/FAO/ WHO 1992).

Arsenic is a carcinogen, according to studies. Multiple human populations exposed largely through inhalation have shown an increase in lung cancer mortality. Additionally, in a population using drinking water with high levels of inorganic arsenic, higher mortality from numerous organ cancers (liver, kidney, lung, and bladder) as well as an increased incidence of skin cancer was identified. (1980, FAO)

#### Acylamino acid fungicides.

Metalaxyl is a fundamental fungicide used to control plant illnesses brought about by Oomycete growths. Metalaxyl is a racemic combination of two isomers, one of which, the R-enantiomer, is the dynamic structure. This enantiomer is the premise of the fungicide, metalaxyl-M (mefenoxam), which is powerful at a large portion of the application pace of metalaxyl. This was created by Syngenta as a trade for metalaxyl, and was essential for a technique to smother conventional rivalry. Metalaxyl's plans incorporate granules, wettable powders, tidies, and emulsifiable concentrates. Application might be by foliar or soil consolidation, surface showering (broadcast or band), soaking, and seed treatment. Metalaxyl enrolled items either contain metalaxyl as the sole dynamic fixing or are joined with other dynamic fixings (e.g., captan, mancozeb, copper compounds, carboxin). Because of its wide range action, metalaxyl is utilized worldwide on an assortment of foods grown from the ground crops. Its viability results from restraint of uridine fuse into RNA and explicit hindrance of RNA polymerase-1. Metalaxyl has both healing and foundational properties. Its mammalian harmfulness is named EPA poisonousness class III and it is additionally generally non-poisonous to most nontarget arthropod and vertebrate species. Metalaxyl is an acylalanine fungicide with fundamental capacity Sukul, P; Spiteller, M (2000). Its substance name is methyl N-(methoxyacetyl)- N-(2,6xylyl)- DL-alaninate. It very well may be utilized to control Pythium in various vegetable yields, and Phytophthora in peas. Metalaxyl-M or Ridomil Gold are trademarks for the optically unadulterated (-)/D/R dynamic stereoisomer, which is otherwise called MefenoxamMonkiedje, Adolphe; Spiteller, Michael (2002).

#### MATERIALS AND METHODS

#### 1-Fungicides used.

The trade name, common name, percentage of active ingredient and type of the tested commerical formulations are shown in Table (1).

Table 1. The tested commerical formulations of mixture of mancozeb with metalaxyl and mixture of copper oxychloride with mancozeb.

Trade name	Formulation types	Active ingredient	Impurities			
Triomax RN.1921	WP	Mancozeb 12%+Copperoxychloride 50%+Cymoxanil 4%	ETU and AS, Cd, Ld			
AcimaxylR.N.3214	WP	Mancozeb 64%+Metalaxyl 8%	ETU and 2,6 Dimethylaniline			

#### 2- Storage stability test:

The tested fungicide formulations were stored at 54 <sup>0</sup>C for 14 days according to FAO Specification (2006), FAO (1992) and FAO (1998). During the storage period, samples were taken at 1, 3, 5, 7 and 14 days to determine the active ingredient and their impurities content for the tested formulations.

### 1-Determenation of active ingredientof ETU (impurities of mancozeb) andby HPLC.

#### HPLC Conditions.

According to Luke et al. (1981) alstrategy, the active ingredient for ETU was evaluated using HPLC apparatus. Quantitative analysis was performed using reverse phase high performance liquid chromotography. In the understudy, an Aglient technologies1200 series HPLC with degasser, quaternary pump, photodiod array detector linked to injection system and computer (model Vectra) was used. The stationary phase consisted of lichrosphere on Rp-8 packed stainless steel column (15 cm x 4.6 mm id) (Table 2).

#### Table 2. HPLC condition for ETU.

Fungicide condition	ETU	
Mobile phase (methanol – ACN-H2O)	25-70-5	
Flow rate ml/min	1	
Wave length nm	235	
Oven temperature	40	
Retention time min	2.753	

#### 1- Determination of active ingredientof ETU HPLC:

Ethylenthiourea (ETU) in Triomax 66% WP andAcimaxyl72% WP were extracted by methanol and evaluated before and after storage for 14 days by HPLC.

## 2- Determination of active ingredient of metalaxyl and its impurities (2,6 dimethyl aniline) by GLC:

#### GLC Conditions.

Agilent 7890B gas chromatograph with autosampler 7693 equipped with Flame Ionization Detector (FID) at250  $^{\circ}$ C, capillary column HP-50+ (30 m x 0.53 mmI.D., 1 µm film thickness). Nitrogen was used as acarrier gas with constant flow 8 ml/min. The oven temperature program was held at 120  $^{\circ}$ C for 1 min, thenramp 20  $^{\circ}$ C /min to 260  $^{\circ}$ C and kept at that temperature for 2 min. Injector temperature was 250  $^{\circ}$ C with splitless mode. The injection

volume was  $1\mu$ l. under these conditions the typical retention time of metalaxyl was 7.767 and for2,6dimethylaniline was 3.165 min. CIPAC 365/TC/M (1992).

#### **3-** Determination of mancozeb.

Decomposition with acid was used to determine the active ingredient % before and after storage. Lead acetate (in the case of mancozeb only) and silver nitrate (in the case of mancozeb modified copper) are used to eliminate hydrogen sulphide. Iodometric titration is used to evaluate how much carbon disulphide is absorbed by methanolic potassium hydroxide. (CIPAC 1973).

#### 4- Determination of Metallic copper.

Cupric ions, formed by digestion with sulphoric acid and nitric acid mixture (50:50 v/v), afforded with potassium iodide, cupreous iodide, were determined before and after storage for 14 days according to (CIPAC 1967) Sodium thiosulphate is used to titrate this one.

#### 5- Determination of heavy metals.

1 gramme copper compound was weighed and transferred to a 150 ml level bottom flask. A mixture of 10 mL sulfuric acid and 15 ml nitric acid was added, and the mixture was slowly evaporated on a soud bath until the white sulfuric acid vapours stopped. A few drops of sulfuric acid were added and allowed to evaporate again. The residue was dissolved in distil water, filtered if necessary, and then transferred to a 300 mL beaker. Ammoia solution was added and stirred until the precipitate that had previously formed dissolved, resulting in a dark blue tone. Ammonia fumes were removed from the solution by boiling it. According to (CIPAC 1970), the sample was cooled to room temperature, cleaned with distilled water, and then moved quantitatively into a 50 ml beaker. Thermo Elemental (Atomic Absorption) is used to determine this. All measurements were taken with a Spectra photometric (model solar M). The instrument software automatically changed the current, wavelength, and slit band width of each element. Using a hydride generation kit, arsenic was determined (model VP 100)

#### 6- Chemcals.

All of the chemicals utilized were reagents of analytic grade. The calibration curves were set using the

standard element solution, which was made from a 1000 mg/L Merck stock solution of the relevant element. 7- kinetic study.

The rate of degradation of the tested active ingredient and half-life period (t 0.5) for the tested pesticides were calculation according to equation Moye et al (1987).

RL t 
$$0.5 = \text{Ln } 2/\text{K} = 0.6932/\text{K}$$
  
K = 1/Tx. Ln a/bx

Where R =Rate of decomposition a = initial residue Tx = time in days bx = Residue at time

#### **RESULTES AND DISSCUSSION**

The usage of ethylene bisdithiocarbamate (EBDCs) fungicides, of which ethylenethiourea is an environmental degradation product, metabolite, and contaminant, is the main source of these studies (IARC 2001). The amount of ethylenthiourea in (EBDCs) fungicide formulations varied depending on the pesticides' storage circumstances, and was raised by increasing temperature, moisture, and storage time. Camoni *et al* (1988), Lentza-Rzosh (1990) and Su Xu (2000). These findings are in agreement with those of Bantoyan and Looker (1973), who discovered that the effect

of storage conditions on the ETU content of formulated (EBDCs) mancozeb was stored for 39 days at 48 <sup>o</sup>C relative humidity of 80%, simulating storage conditions that might occur in everyday work during the summer. After 39 days of capacity, the initial ETU content in mancozeb formulation increased. Furthermore, Mcewen and Stphenson(1979) discovered that ETU may be created when EBDCs were used on stored food, as well as when fruit or vegetables with residues of these fungicides were cooked.

Data in Table (3) indicated that active ingredient of mancozeb in Acimaxyl was 64% before storage and became 56.55% after 14 days of storage at 54 <sup>o</sup>C also that data illustrated that 2,6 dimethylanline impurity in metalaxyl was 0.020% before exposure of storage and increased to become 0.040% after 14 days of storage. In addition, the results indicated that storage and the increasing percent was in content ethylenthiourea and 2,6dimethylaniline impurities in Acimaxy172% WP were blower matching the maximum level (0.5% and 0.1%) for ETU and 2,6 dimethylaniline defined by FAO Specification (1992,1980) respectively in Acemaxil 72% WP. whereas the calculated half – life values of mancozeb and metalaxyl were 149.48 and 43.33 days respectively.

Table 3. Effect of storage thermal stability of mancozeb and its impurities ethylenthiourea (ETU) and metalaxyl and its impurities 2,6 dimethylaniline in Acimaxyl 72% WP formulation at 54 °C.

Storage periods Mancozeb64% content			Mancoz	eb impurities	Metalaxyl	8% content	Metalaxyl impurities			
Days	Mancozeb	Loss %	ETU %	Increase%	Metalaxyl	Loss %	2,6 dimethylaniline %	e % Increase%		
Initial	64	0.00	0.113	0.00	8	0.00	0.020	0.00		
1	63.85	0.23	0.119	5.31	7.82	2.25	0.025	25		
3	63.70	0.47	0.133	17.70	7.70	3.75	0.028	40		
5	63.22	1.22	0.149	31.86	7.54	5.75	0.031	55		
7	62.5	2.34	0.170	50.44	7.49	6.375	0.037	85		
14	56.55	11.64	0.222	96.46	7.22	9.75	0.040	100		
T 0.5	149.48				43.33					

Initial = one day before storage.

Mancozeb and ETU had a lesser persistence, and this information was observed in the soil, resulting in a rapid rate. The time it took to degrade mancozeb and define ETU was increased to 30 days. HanumantheraJu and Awasthi (2004), Alamwaini *et al* (2012).

# Effect of thermal storage at 54 <sup>o</sup>C on stability of mancozeb, metallic Copper and their impurities in Triomax 66% WP.

Data in Table (4) indicated that (a.i %) of mancozeb in Triomax was 12 % before storage and became 11.33 % after 14 days of storage at 54  $^{\circ}$ C. Also the data indicated that thermal storage at 54  $^{\circ}$ C shows breakdown of ETU in Triomax which was 0.115 % before storage and became 0.160 % after 14 days storage.

The synthesis of ETU by thermal degradation of ethylene bis (dithiocarbamate) in fluid media was considerably reduced by the addition of copper salts, according to Suzanne Losage (1980). In the presence of CuSo4 and copper, the assessment of CS2 and the breakdown of maneb or maneb were reduced, resulting in the development of a stable cupric ethylene bisthiocarbamate) complex.

Copper modifided mancozeb (the response result of manganese ethylene bisdithiocarbamate and soluble zinic ion) and processes for making it, which result in a product that reduces the generation of ethylenethiourea (ETU) during long-term storage, decreases the solubized ethylenthiourea produced during the manufacture or storage of mancozeb, and increases the fungicidal action of mancozeb. The findings show that dithiocarbamate is formed from a liophilic complex with di and trivalent metallic elements, which is held together by the sulphur atom present in dithiocarbamate molecules (Sachinidis and Award 1981).The results showed that the level of arsenic and cadmium before and after storage in copper modified mancozeb were in accepted limits according to FAO (1989 and 1998).

Several pesticides are thought to have carcinogenic effects. According to its chemical structure, the minor component might be associated to ligaud, colloids, or particles of natural and inorganic forms. Best and Doglido (1994). Despite the fact that the finished product is affected not only by the major mineral source, but also by trace elements present during pesticide production. The manufacturing of pesticide is another important usage of mercury and arsenic (Hutton and Symon, 1986).

Temperature is known to be one of the most important factors influencing the stability, persistence, and degradation of pesticides, with the chemical reaction rate doubling for every 10  $^{0}$ C increase in temperature and decreasing for each 10  $^{0}$ C drop in temperature, according to State (1990) and Suett (1979). The data presented in Table (4) show the effect of storage at 54 ±2 $^{0}$ C on the

stability of metallic copper active ingredient in Triomax 66%. The data indicate that metallic metallic copper (a.i) was relatively stable whereas the percentage losses of metallic copper were 0.79, 1.59, 2.31, 3.34 and 5. These results indicated that copper formulation was passed successfully and comply with FAO specification (1989 and 1998). These results are similar obtained by Abd El-Aal *et al* (1993) and El Deep *et al* (1991), who reported that correlation between temperature and storage temperature and decomposition of pesticides formulation. The results also showed the level of cadmium and arsenic was in allowed limited according to FAO (1989 and 1998).

In addition, the Triomax data demonstrate a rise in the amount of lead after storage due to the metal cation and ligand in a complex acting as an electron acceptor and donor, respectively. The term "soft" refers to the species' electron cloud being malleable or polarizable, as well as the electrons being mobile and easily manipulated. Covalent bonding is something that soft creatures tend to do. Hard species are relatively rigid and non-deformable, have poor polarizability, tightly hold their electrons, and tend to form ionic connections in complex formation (Langmuir 1997). This indicates that when the amount of Pb complexing grows, the total Pb concentration must likewise rise to achieve lead saturation equilibrium. To put it another way, metal complexing boosts overall metal solubility (EPA 2007). Some pesticides are suspected of having cancer-causing effects. According to its chemical structure, the trace element might be coupled with ligands, colloids, or organic and inorganic particles. (Best and Doglido, 1994); Insecticides, herbicides, and fungicides will all be categorised as pesticides. Although the final product is likely to be affected not only by the supply of primary minerals but also by trace elements included during pesticide production, the pesticides are administered as solid (powder) and liquid (concentrate water solution).

Storage period	Mancozeb 12% ETU		Copper 29%			Pb	Cd				AS				
(days)	%	Loss %	%	Increase	%	Loss	mg/ I	Increa	FAO	mg/	Increase	FAO	%	Increase	FAO
				%	<sup>70</sup> %	kg	se%	Max	kg	%	Max	mg/kg	%	Max	
Initial	12	0.00	0.115	0.00	29	0.00	97	0.00	145	7.99	0.00	29	2.99	0.00	29
1	11.90	0.83	0.119	3.48	28.77	0.79	105	8.25	143.85	8.05	0.75	28.77	3.01	0.67	28.77
3	11.87	1.08	0.121	5.22	28.54	1.59	126	29.90	142.7	8.11	1.50	28.54	3.04	1.67	28.54
5	11.79	1.75	0.129	12.17	28.33	2.31	147	51.55	141.65	8.22	2.88	28.33	4.11	37.46	28.33
7	11.60	3.33	0.139	20.87	28.03	3.34	160	64.95	140.15	8.31	4.01	28.03	4.55	52.17	28.03
14	11.33	5.58	0.160	39.13	27.55	5	180	85.57	137.75	8.40	5.13	27.55	5	67.22	27.55
T0.5	113.64				104.24										

Initial = one day before storage.

FAO maximum (Cd) = 0.1 x b mg/kg where b copper content by g/kg

#### CONCLUSION

The percentage of ETU decrease in mancozeb compounds which contain copper than mancozeb compounds modified metalaxyl.

#### REFERENCES

- "A Short History of Fungicides" (2016): The American Phytopathological Society. Archived from the original on 16 April 2016. Retrieved 10 May 2016.
- "Gowan buys Dow's Gavel potato fungicide" (2008): grainews.ca. July 18, 2008.
- "Mancozeb".Cornell University( 1993): Retrieved 2014-07-20. It is a combination of two other chemicals of this class, maneb and zineb
- Abd El Aal. F; A.G EL\_Sisi; M.A. EL-Hamaky and Y.S. Ibraheim (1993): The influence of paking and storage conditions on the physical and chemical stability some pesticides formulations. Egypt. J. Appl. Sce. 8 (9):499- 508.
- Alamwain, A; H, S Rewal ; S, Sanjay ; S, Balwinder and J. AwadBhat (2012): Persistence of metalaxyl and mancozeb on potato leaves and their residue in tubers Pakistan, Journal of biological science, 15:44-48.
- Andreu V and Gimeno-Garcia E. (1999): Evolution of heavy metals in marsh areas under rice farming. Environmental Pollution, 104, 271-282.
- Bantoyan, W. R and J. B Looker (1973). Degradation of commerical ethylene bisdithiocabamate formulation to then thio urea under evaluated temperature and humidity J. Agric. Food Chem. 21(3): 338-314.

FAO maximum (Pb) = 0.5 x b mg/kg where b copper content by g/kg FAO maximum (As) = 0.1 x b mg/kg where b copper content by g/kg

- Camoni.I, D. Muccio, A. Pontecorvo, D. C. Hip (1988): Survey of ethylenethiourea (ETU) in ehylenebis (dithiocarbamate (EBDC) fungicides.Ecotoxicol Environ. Saf 16 (2) 176-179.
- CIPAC (1967): Reised 1974 prepared by British Committee Of PAC-Chairman H crossely (the murphy chemical co ltd.)
- CIPAC (1970): Collaborative internation pesticides analytical council limeted), P 226-228, 236, 238, 637, 1170.
- CIPAC (1973): Provisional method, prepared by dithiocarbamate panel of PAC-UK ChaimanAstevenson (robinson bros 1 td det of heavy metals).
- CIPAC 365/TC/M.; (1992): Metalaxyl Technical; Vol., E, p. 123-130
- Doglid,O and G Best (1994): Chemistry of water and water pollution Ellis harwood; New York, pp 362.
- El-Deep, W.H ; M.K El-Shemy and Y.S. Ibrahim (1991): Effect of storage temperature on the stability, biological activity and phytotoxicity of certain insecticides. Fourth Arab congress plant protection Cairo 1-5 Dec., P399- 403.
- EPA (2007): Environmental Protection Agency. U.S. Framework forMetals Risk Assessment.
- FAO (1980): Tentative specification for plant protection products, Rom, Italy.
- FAO (1989): FAO Specification group on pesticides specification registration requirement and application Standards Pp: 15-17 and 23-25: copper oxychlorid cupric sulfate – cuprous oxid.

- FAO (1992): Specification, metalaxyl wettable powder 365/WP/S/F.
- FAO (1998): FAO Specification, copper hydroxide wettable powders 44 WP/S/F.
- FAO (2006): Specification, guidelines for soiled formulation.Roma, Italy specification.
- FAO 1980: FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS Rome, 1980AGP: CP / 85.
- FAO/WHO (1968): Evaluations of some pesticide residues in food FAO/PL: 1968/M/11/1; WHO/Food Add./68.30
- HanumantheraJu, T. H; M. D, Awasthi, (2004): Persistence and degradation of metalaxyl, mancozeb fungicides of Envirmental Science and Indian Journal of Envirmental Engineering. 11 2004; 46 (4):321-321.
- Hutton, M; C,Symon, (1986):The quantities of cadmium, lead, mercury and arsenic entering the UK. Environment form human activates. Sci. Total environmental.
- IARC (International Agency for Research on Cancer) (2001): Monographs, vol. 79, spmethyrotropic Agent Agents IARC-Lyon, France, PP 659-701.
- Langmuir, D. (1997): Aqueous environmental chemistry. Upper Saddle River, NJ: Prentice-Hall.
- Latijnhouwers, M.; de Wit, P.J. and Govers, F. (2000): Oomycetes and fungi: similar weaponry to attack plants. Trends in Microbiology. Vol., 11: 462-469.
- Lentza- Rzosh (1990): Ethylenthio urea (ETU) in relation to use of ethylene bisdithiocarbamate (EBDC) fungicides Rev. Environment Contamination Toxicology 115- 1-39.
- Luke,M; M, D. Jerry; and T. M Herbet (1981): improved multresidue gas chromatographic determination, organophosphophours and organ halogen pesticidesin procedure, using flam photometric and electrolytic conductivity detectors. J. Asso. Off. Anal chem., 64 (5):1187-1195.
- Mcewen, F. L and G.R Stphenson (1979): The use and significance of pesticides in the environment. N,Y John wiley and sons Inc.
- Monkiedje, Adolphe; Spiteller, Michael (2002): Effects of the phenylamide fungicides, mefenoxam and metalaxyl, on the microbiological properties of a sandy loam and a sandy clay soil". Biology and Fertility of Soils. 35 (6): 393–398. doi:10.1007 /s 00374 - 002-0485-1. S2CID 2264 2870.

- Moye, H.A; Y Malagodi.; G. L Leibe and P.G Wislocki, (1987): Residues of avermectin B1a potation crop and soils following soil treatment with (C14) Avermectin B1a. J Agric. Food chem. 35, 859-864.
- permitting application of copper fungicide of the Soil Association Archived 15 October 2009 pollution; Ellis Harwood; New York, 2009; 362pp.Saddle River, NJ: Prentice-Hall.
- Sachinidis, J and M, W V,Grant (1981): Metal exchange reaction between divalent metal ions and their dithiocarbamate complexes in dimethyl sulfoxide a kinetic and mechanistic study Australian Journal of chemistry. 34 (10): 2195- 2215.
- Schneiderhan, F. J. (1933): The discovery of Bordeaux mixture. Phytopathological Classics, Number 3: 1-25.
- Soil Association Organic Standards for Producer (2010), Version 16.1, April, Section 4.11.11,2010
- State, K (1990): Kanas State University Agricultrual Experment Station and Coopererativeextention service.Factors affecting pesticide behavior and breakdown formulation. May: 1-8.
- Su Xu (2000): Environmental fate of mancozeb environmental monitoring of pest management department of pesticides regulation sacrement CA 95814-3510:1-9.
- Suett, D.L (1979): Persistance and degradation of chlorfenvinphoschlormephos, disulfotonphorate and primiphos-methyl flowing spring and late summer soil application.Pestic. Sci., 6 385-393.
- Sukul, P; Spiteller, M (2000): "Metalaxyl: persistence, degradation, metabolism, and analytical methods". Reviews of Environmental Contamination and Toxicology. 164. PMID 12587832.
- Suzanne, L, Osag (1980): Reduction of the formation ethylene thio urea from ethylenbis (dithiocarbamate by Cu +2. J AgricChem, 28: 787-790.
- UNEP/FAO/WHO (1992): United Nations Environment programmer The Contamination of food environment library. No. 5.
- UNEP/FAO/WHO 1986: Summary of 1980 83. Monitoring data, joint food contamination monitoring program, Geneva, WHO.
- Zwieten M. V.; G. Stovold and L. V. Zwieten(2007): Alternatives to copper for disease control in the Australian organic industry. A report for the Rural Industries Research and Development Corporation. http://www.rirdc.gov.au/ full reports/index.html

دراسه ثبات بعض المبيدات الفطريه وشوائبها المصاحبه لها فى بعض الظروف البيئيه ايمن سميح عريبى سلومه قسم بحوث تحليل المبيدات – المعمل المركزي للمبيدات –مركز البحوث الزراعيه – الدقي الجيزه- مصر

تم در اسة تأثير ظروف التخزين على بعض مبيدات الفطريه، ميتالاكسيل المضاف اليه ماتكوزيب ممثلة في اسيماكسيل ٢٧% مسحوق قابل للبلل، والنحاس المضاف اليه الماتكوزيب ممثلا في تر ايوماكس ٦٦% مسحوق قابل للبلل. أظهرت النتائج أن معدلات التحلل لأسيماكسيل ٢٧٪ WP و تر ايوماكس ٦٦% مسحوق قابل للبلل، والنحاس المضاف اليه كانت قيم نصف العمر المحسوبة للأسيماكسيل (١٤٩,٤٨ يومًا للماتكوزيب و ٣,٣٣ يومًا للميتالاكسيل) و (١٣,٦٢ يومًا للماتكوزيب و ٢٠٤،٤ WP في تر يوماكس ٦٤% WP في تر يوماكس ٦٤% السوماكس ٢٤٪ على بعد التحزين ١٤ يومًا عند ٢٤ درجة مئوية ، تم رفع تأثير التخذين الحراري على تخليق الإيثيلين ثيوريا (ETU) في الماتكوزيب و ١٠٤,٠٪ بلا معران مالتكوزيب و ١٠٤,٠٪ في الماتكوزيب و ١٠٤,٠٪ في بعد التحزين ١٤ يومًا عند ٢٤ درجة مئوية ، تم رفع تأثير التخزين الحراري على تخليق الإيثيلين ثيوريا (ETU) في الماتكوزيب و ١٠٤,٠٪ لأسيماكسيل و ٢٠,٠٪ للتر يوماكس. علاوة على ذلك ، كان تأثير درجة حرارة الفرن على التخزين الحراري على تخليق الإيثيلين ثيوريا (ETU) في الماتكوزيب إلى ٢٢،٠٪ لأسيماكسيل و ٢٠,٠٪ للتر يوماكس. علاوة على ذلك ، كان تأثير درجة حرارة الفرن على التخزين ٢,٦ شوائب ثناتي ميثيل أنيلين في الأسيماكسيل (ماتكوزيب ٢٤٪ ولمع / ٢٠,٠٪ في التخزين و ٢٠٤٠٠٪ في نهاية وقت تخزين التجربة. قبل وبعد التخزين عند ٢٤ درجة مئوية ، تم قياس مستويات الرصاص والكادميوم والزرنيخ (ملغم / كنم) وكنك النحاس المحني في تريوماكس ٦٦٪ (ماتكوزيب ٢٢٪ ، والنحاس ٢٣). كانت مستويات الكادميوم والزرنيخ أقل من حدود منظمة الأغذية والزراعة ، بينما كان الرصاص أعلى من حدود المنظمة. أظهرت البيانات أن النحاس المعدني في مستحضر التر ايوماكس ظل ثابيًا بشكل عام بمرور الوقت